

**PATENT**  
**Docket No. 6479**

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**APPLICATION FOR UNITED STATES LETTERS PATENT**

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**TITLE:**

**PROCESS FOR BURNING SULFUR-  
CONTAINING FUELS**

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## **PROCESS FOR BURNING SULFUR-CONTAINING FUELS**

### **CROSS REFERENCE TO RELATED APPLICATION**

This application claims the benefit of U.S. Provisional Application No. 60/460,680, filed April 4, 2003.

### **BACKGROUND OF THE INVENTION**

#### **Field of the Invention**

This invention relates to the field of burning sulfur-containing fuels and to reducing the production of SO<sub>x</sub> and NO<sub>x</sub> therein.

#### **Related Art**

Over the past several years, power generation processes and other combustion processes for burning sulfur-containing fuels have been subject to increasingly strict emissions restrictions, particularly for NO<sub>x</sub> and SO<sub>x</sub>. Sulfur-containing fuels that are popular for power generation but especially problematic for emissions include coal, petcoke and heavy fuel-oil boilers. Current methods of removing SO<sub>x</sub> from, *e.g.*, coal fired boilers are very expensive. It is anticipated that within a few years, most of those boilers in the U.S. will require de-sulfurization equipment. NO<sub>x</sub> removal techniques are similarly expensive, complex and difficult to operate. The preferred embodiments of the present invention disclose cost-effective methods to remove SO<sub>x</sub> and NO<sub>x</sub>.

Thus, a problem associated with processes for burning sulfur-containing fuels that precede the present invention is that they produce a level of SO<sub>x</sub> emission that is unacceptable in view of existing environmental regulations.

Yet another problem associated with processes for burning sulfur-containing fuels that precede the present invention is that they produce a level of NO<sub>x</sub> emission that is unacceptable in view of existing environmental regulations.

Still another problem associated with processes for burning sulfur-containing fuels that precede the present invention is that they have not been successively modified to provide adequate

combustion characteristics resulting in adequate reduction of  $\text{SO}_x$  formation sufficient to meet environmental guidelines without expensive and complex  $\text{SO}_x$  treatment apparatus, such as scrubbers, etc.

Another problem associated with processes for burning sulfur-containing fuels that precede the present invention is that they have not been successively modified to provide adequate combustion characteristics resulting in adequate reduction of  $\text{NO}_x$  formation sufficient to meet environmental guidelines without expensive and complex  $\text{NO}_x$  treatment apparatus.

An even further problem associated with processes for burning sulfur-containing fuels that precede the present invention is that they have not been provided with a means for chemically preventing the formation of  $\text{SO}_x$  and concurrently provided with a mechanism to avoid problems associated with slagging or other fouling of the combustion equipment.

Another problem associated with processes for burning sulfur-containing fuels that precede the present invention is that they have not been provided with a means for chemically preventing the formation of  $\text{NO}_x$  and concurrently provided with a mechanism to avoid problems associated with slagging or other fouling of the combustion equipment.

For the foregoing reasons, there has been defined a long felt and unsolved need for a process for burning sulfur-containing fuels that facilitates an inexpensive, non-intrusive method for reducing the formation of  $\text{SO}_x$  while at the same time maintaining the operability and safety of the combustion process.

### **SUMMARY OF THE INVENTION**

A process for burning a sulfur-containing fuel to produce a flue gas is disclosed. The process comprises introducing a sulfur-containing fuel into a combustion chamber, introducing at least one oxygen enriched oxidant stream into the combustion chamber, and introducing potassium carbonate into the combustion chamber. The sulfur-containing fuel is burned to produce the flue gas and potassium sulfate.

An object of the present invention is to provide a process for burning sulfur-containing fuels that produces a level of  $\text{SO}_x$  emission that is within acceptable levels in view of existing environmental regulations.

Yet another object of the present invention is to provide a process for burning sulfur-containing fuels that produces a level of  $\text{NO}_x$  emission that is within acceptable levels in view of existing environmental regulations.

Still another object of the present invention is to provide a process for burning sulfur-containing fuels that can be successively modified to provide adequate combustion characteristics resulting in adequate reduction of  $\text{SO}_x$  formation sufficient to meet environmental guidelines without expensive and complex  $\text{SO}_x$  treatment apparatus, such as scrubbers, etc.

Another object of the present invention is to provide a process for burning sulfur-containing fuels that can be successively modified to provide adequate combustion characteristics resulting in adequate reduction of  $\text{NO}_x$  formation sufficient to meet environmental guidelines without expensive and complex  $\text{NO}_x$  treatment apparatus.

An even further object of the present invention is to provide a process for burning sulfur-containing fuels that provides a means for chemically preventing the formation of  $\text{SO}_x$  and concurrently provides a mechanism to avoid problems associated with slagging or other fouling of the combustion equipment.

Another object of the present invention is to provide a process for burning sulfur-containing fuels that provides a means for chemically preventing the formation of  $\text{NO}_x$  and concurrently provides a mechanism to avoid problems associated with slagging or other fouling of the combustion equipment.

These and other objects, advantages and features of the present invention will be apparent from the detailed description that follows.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

In the detailed description that follows, reference will be made to the following figures:

Fig. 1 is a schematic illustration of a first preferred embodiment of a process for burning a sulfur-containing fuel;

Fig. 2 is a schematic illustration of a second preferred embodiment of a process for burning a sulfur-containing fuel;

Fig. 3 is a schematic illustration of a third preferred embodiment of a process for burning a sulfur-containing fuel; and

Fig. 4 is a graph illustrating data of theoretical data expected from burning a sulfur containing fuel according to a preferred embodiment of a process for burning sulfur-containing fuel.

## **DESCRIPTION OF PREFERRED EMBODIMENTS**

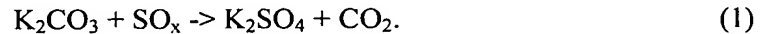
In its simplest application, a process for burning a sulfur-containing fuel to produce a flue gas is disclosed. The process comprises introducing a sulfur-containing fuel into a combustion chamber, introducing an oxidant stream into the combustion chamber and mixing it with the sulfur-containing fuel to define a combustion zone, and introducing potassium carbonate into the combustion chamber. The sulfur-containing fuel is burned to produce the flue gas and potassium sulfate.

In the preferred embodiments, a combustion subassembly uses at least two, and sometimes three, oxidant streams. In the example in which coal is the sulfur-containing fuel, oxygen enrichment is employed to reduce  $\text{NO}_x$ , as is more fully described in applicant's U.S. Patent Application Serial No. 10/ (from S-6415), filed 15 January 2004, hereby incorporated by reference.

In the preferred embodiments, a process designed to reduce  $\text{SO}_x$  emissions in boilers,

particularly in coal-fired boilers, is disclosed. The process includes introducing potassium carbonate in the combustion process, at the burner level or above the burners. When used in conjunction with oxygen enrichment, NO<sub>x</sub> reduction can be achieved, to an even greater degree than is expected by using oxygen enrichment alone. By this process, SO<sub>x</sub> levels can be reduced to a few ppm, even for high-sulfur fuels such as Midwestern coals and pet coke. At the same time, the NO<sub>x</sub> reducing effect of the oxygen enrichment is enhanced by the potassium carbonate, resulting in a low NO<sub>x</sub> process. To avoid slagging effect of the high temperature on the potassium carbonate, a staged combustion process is most preferred.

Laboratory test data illustrates just a portion of the expected benefits in removing sulfur from pet-coke combustion using potassium carbonate. Test results show that the flue gas of both air-combustion (traditional) and oxy-combustion (oxygen enriched) contained approximately 6 ppm SO<sub>x</sub>. This is extremely low in view of the fact that the pet-coke used contained approximately 3-6% sulfur. The reaction taking place in the combustion process is:



Recent calculations made of the adsorption of SO<sub>2</sub> by K<sub>2</sub>CO<sub>3</sub> in a pulverized coal boiler fired with Illinois No. 6 coal are illustrated as follows. It was assumed that one million pounds per hour of coal, corresponding to approximately 1000 MW power production, was to be burned with 10% excess air. An elemental composition of the parent coal reveals:

Element	Wt% daf
C	77.32
H	5.33
N	1.49
O	8.88
S	6.98

The coal was assumed to have 10% ash, and moisture was neglected. Note that the sulfur composition for this coal is high (approximately 7 wt.% daf). The adsorption rate was assumed to be limited by the diffusion of SO<sub>2</sub> to the surface of the particle. The mass transfer rate is:

$$\dot{N}_{SO_2}'' = h_m (C_{SO_2,g} - C_{SO_2,s}) \quad (2)$$

where  $\dot{N}_{SO_2}''$  is the molar flux of  $SO_2$  to the particle surface per external surface area of particle,  $h_m$  is the convective mass transfer coefficient, and  $C_{SO_2}$  is the concentration of gas in either the bulk gas phase or at the surface. Under diffusion-limited conditions,  $C_{SO_2,s}$  is essentially zero, and equation (2) becomes very simple. The mass transfer coefficient is calculated from the Sherwood number, which is 2.0 for small particles:

$$Sh = \frac{h_m d_p}{D_{SO_2-air}} \quad (3)$$

where  $d_p$  is the particle diameter, assumed to be 50 microns in this calculation. The diffusivity of  $SO_2$  was calculated from the Chapman-Enskog theory for kinetic gases. The parameters for air were used, since they are similar to post-combustion gases. The diffusivity changes as a function of temperature.

For this calculation, a temperature profile was assumed. The particle and gas temperature started at 2000 K and then decreased in a linear fashion to 1000 K after one second. This is thought to approximate the conditions in most pulverized coal boilers.

The initial concentration of  $SO_2$  was calculated from the flow rates of coal and air, assuming that all of the sulfur in the coal ended up as  $SO_2$ . This yielded a calculation of about 4510 ppm. The differential equation for the change in  $SO_2$  concentration in this case is:

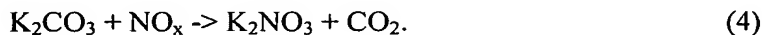
$$\frac{dC_{SO_2}}{dt} = n_p A_p \dot{N}_{SO_2}'' \quad (3)$$

where  $n_p$  is the particle number density (number of particles per cubic meter),  $A_p$  is the external area per particle ( $4\pi r_p^2$ ), and  $\dot{N}_{SO_2}''$  is from equation (2).

The resulting SO<sub>2</sub> profile is shown in Fig. 4. As shown, the calculations showed only 70% conversion of SO<sub>2</sub> to K<sub>2</sub>SO<sub>4</sub>. Actual laboratory data from petroleum coke yield much better results, however. The data indicates a conversion of greater than 95%. Although the reason for the difference is not fully understood, it is believed that perhaps some of the potassium species may have vaporized, which would increase conversion of SO<sub>2</sub> (because diffusion to a particle surface would not be necessary).

It is further believed that using K<sub>2</sub>CO<sub>3</sub> particles will facilitate adsorbing the SO<sub>2</sub> from hot post-flame gases. Although, in a preferred embodiment described herein, K<sub>2</sub>CO<sub>3</sub> is injected with the coal, it is possible that this arrangement will cause the K<sub>2</sub>CO<sub>3</sub> to become too hot. Excessive temperatures are expected to the K<sub>2</sub>CO<sub>3</sub> to melt and perhaps become sticky, therefore causing a deposition problem in the combustion chamber. However, because the data seem to indicate that there may have been some vaporization and consequent enhancement in the sulfur conversion to sulfur carbonate, it is possible that the vaporization may be beneficial.

In a more preferred embodiment, the K<sub>2</sub>CO<sub>3</sub> is injected above the flame zone (primary combustion zone) in order to reduce fouling effects downstream. Thus, in the preferred embodiment illustrated in Fig. 3, potassium carbonate is introduced with the tertiary air, in a second combustion zone. Not only does this arrangement overcome the slagging of potassium carbonate that may occur when it is introduced directly into the flame, it provides an enhanced NO<sub>x</sub> reduction. The data suggests that NO<sub>x</sub> formation is decreased by the addition of the potassium carbonate, in a reaction of the type:



The mechanism by which this NO<sub>x</sub> reaction occurs is not fully understood. However, in combination with the oxygen enrichment, this preferred embodiment seems to yield synergistic results.

Referring now to Figs. 1 through 3, three preferred embodiments of a burner are shown in schematic fashion. As shown schematically in Fig. 1, a combustion chamber 20 is shown



having a first or primary combustion zone 22 and a second or secondary combustion zone 24. The first of the three inlet streams, the primary stream 26, combines the primary oxidant air with the solid, pulverized fuel, and thereby conveys the pulverized solid fuel into the combustion chamber 20 in the primary combustion zone 22. In an application where the fuel is not solid, the primary inlet stream can be eliminated. The secondary stream 28 introduces the secondary oxidant into the burner, around or near the primary stream 26, and into the primary combustion zone 22. The tertiary stream 32, is injected, if necessary, in the secondary combustion zone 24, to complete combustion. It is understood that in these apparatus, multiple air streams of each type thus described (primary, secondary and tertiary) can be utilized – indeed multiple burners can be used; the following description will refer to each in the singular for simplicity).

As shown in Fig. 1, oxygen enrichment is employed in the primary and secondary oxidant streams, and the potassium carbonate is introduced with the fuel. As shown in Fig. 2, oxygen enrichment is employed in all three oxidant streams, and the potassium carbonate is introduced with the fuel. As shown in Fig. 3, oxygen enrichment is employed in all three oxidant streams, and the potassium carbonate is introduced with the tertiary oxidant into the secondary combustion zone.

Flue gas 34 is formed and exhausted from the combustion chamber 20. Thus, the first combustion zone is the zone where the fuel reacts around the burner level. Secondary zones are sometimes desirable if  $O_2$  is provided downstream from the burner before the furnace exit to provide more complete combustion downstream. The oxygen equivalent amount of oxidant is adjusted in the oxidant streams (primary, secondary and, if applicable, tertiary oxidant) to maintain a predetermined amount of excess oxygen in view of the stoichiometric balance needed to complete combustion. This amount of excess oxygen is preferably maintained so that the  $O_2$  content of the flue gas is maintained between 1.5 percent and 4.5 percent, and more preferably between 2.5 percent and 3.5 percent, and most preferably about 3.0 percent. For purposes of this application, all  $O_2$  contents are stated by volume of dry gas (excluding  $H_2O$ ).

Thus, the preferred embodiments disclose processes designed to reduce  $NO_x$  and  $SO_x$  emissions in boilers, particularly in coal-fired boilers. These embodiments comprise introducing potassium carbonate in the combustion process, at the burner level or above the

burners, in conjunction with oxygen enrichment. By using this process, the  $\text{SO}_x$  levels can be reduced to a few ppm, even for high-sulfur fuels such as Midwestern coals and pet coke. At the same time, the  $\text{NO}_x$  reducing effect of the oxygen enrichment will be significantly enhanced by the potassium carbonate, resulting in a low  $\text{NO}_x$  process. Due to the slagging effect of the high temperature on the potassium carbonate, a staged combustion process may be preferred. Potassium sulfate can be scrubbed from the flue gas and can be sold as a fertilizer.

Fig. 1 illustrates a first preferred embodiment. The boiler using a solid fuel, such as pet-coke or coal, and utilizes three oxidant streams – primary for fuel transport, secondary for combustion, and tertiary for staged combustion. Note that, as adapted to a liquid fuel-burning apparatus, the primary oxidant stream may be unnecessary.

As shown, the process works to reduce  $\text{NO}_x$  emissions by controlling temperature at the burner level, and further due to the introduction of the potassium carbonate in the boiler at the same level with the fuel. By controlling the temperature and limiting it from becoming too high, to avoid  $\text{NO}_x$  production, potassium carbonate slagging will be reduced or perhaps completely avoided. Oxygen is injected at the primary/secondary oxidant level, in order to initiate the combustion process faster and more efficient than with air alone (particularly under fuel-rich conditions).

It is noted that, as less air will be used at the primary/secondary oxidant level, the combustion will be less efficient. Under these circumstances, oxygen offers a clear way to balance this effect, due to the enhanced reactivity when compared to air combustion. Additionally, the presence of the oxygen in the primary combustion zone is even more desirable when low-volatile fuels are implemented, such as anthracite or pet-coke. Finally, the use of an oxygen-enriched oxidant in the primary combustion zone will heat the fuel quicker, and will allow the nitrogen to be released in pure form, rather than being transformed in nitric oxide.

The preferred embodiment illustrated in Fig. 2 shows an alternative process for improving combustion efficiency by improving the oxygen-fuel mixing at the burner level between the

fuel and oxidant. In the embodiment of Fig. 2, oxygen enrichment is introduced at the tertiary oxidant level as well, to enhance combustion at the secondary combustion zone.

Referring now to Fig. 3, potassium carbonate is injected into the boiler at the tertiary oxidant level. By injecting the potassium carbonate in the secondary combustion zone, the higher-temperature environment at the burner level is avoided. The potassium carbonate can be injected through the air stream, or even better, through the oxygen stream (where an oxygen lance is used), due to the higher flow velocities, yielding better mixing with the flue gas stream. Alternately, oxygen can be introduced only at the primary/secondary oxidant level, for  $\text{NO}_x$  control.

It is preferred that the quantities of potassium carbonate used be selected to comport with the stoichiometry defined by the sulfur content in the fuel. In a preferred embodiment, the potassium carbonate is introduced into the combustion chamber in an amount sufficient to exceed the stoichiometric requirement needed to react with the sulfur in the fuel by between about 0% and about 50%. In a more preferred embodiment, the excess is between about 10% and about 50%. In a most preferred embodiment, the excess is between about 20% and about 35%. As shown by the data, the process results in at least half of the sulfur in the sulfur-containing fuel being converted to potassium sulfate. Oxygen is used such as to replace less than 10-20% of the overall oxidant, in a relationship between the primary/secondary oxidant stream and tertiary stream such as to minimize the  $\text{NO}_x$  formation and unburnt fuel in the ash.

Thus, in a preferred embodiment, a process for burning a sulfur-containing fuel to produce a flue gas is disclosed. A sulfur-containing fuel is introduced into a combustion chamber at a fuel inlet. A primary oxidant stream containing more than 21% oxygen is introduced into the combustion chamber at a primary oxidant inlet positioned proximate to or coincident the fuel inlet and mixing it with the sulfur-containing fuel to define a first combustion zone. A secondary oxidant stream containing more than 21% oxygen is introduced into the combustion chamber at a secondary oxidant inlet positioned so that the secondary oxidant enters the combustion chamber in the primary combustion zone. A tertiary oxidant stream containing more than 21% oxygen is introduced into the combustion chamber at a tertiary oxidant inlet

positioned away from the primary oxidant inlet and away from the secondary oxidant inlet. The tertiary oxidant enters the combustion chamber to define a secondary combustion zone.

The total oxygen content of the oxidant entering the combustion chamber exceeds 21%. Potassium carbonate is introduced into the combustion chamber through the tertiary air inlet in an amount sufficient to exceed the stoichiometric requirement needed to react with the sulfur in the fuel by between 0% and 50%. The sulfur-containing fuel is burned to produce the flue gas and potassium sulfate. At least half of the sulfur in the sulfur-containing fuel is converted to potassium sulfate.

While in the foregoing specification this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for purpose of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.